International Journal of Computational and Experimental Science and Engineering (IJCESEN)
Vol. 1-No.1 (2015) pp. 36-38

www.ijcesen.com

Special Issue for "International Conference on Computational and Experimental Science and Engineering" (ICCESEN-2014)"

Spectroscopic and Statistical Methods Used to Compare the Elemental Composition of Historical Samples

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Keywords
spectroscopy,
elemental composition,
multivariate analysis

Abstract: For different purposes in investigation of cultural heritage samples, including ancient coins, it is necessary to use non-destructive and/or almost non-invasive spectroscopic techniques in combination with appropriate statistical methods.
In this paper, we want to show some similarities and certain differences in the elemental composition of two bronze coins, produced for use in the same geographical area, but at different historical moments. We choose the experimental method of laser ablation or laser induced breakdown spectroscopy (LIBS) as well as two emission spectroscopy of x-rays, excited using radioactive source, or x-ray tube. Finally, in qualitative and quantitative interpretation of the multitude of data obtained by LIBS experiment, we used two methods of multivariate analysis, as follow: Principal component analysis (PCA) and Partial least squares (PLS) methods.

1. Introduction

The development of non-destructive analytical methods, increased interest in exploring elemental composition of high – quality samples from cultural heritage, including coins, especially those of ancient origin. Due to its non destructiveness and relatively quick to results, in numismatic research of sample surface, quite often used methods are XRF [1,2], PIXE [3], and Raman or micro-Raman spectroscopy [4,5]. Furthermore, the widespread use of lasers in recent years has enabled the development of almost non-destructive methods suitable for in depth analysis, so that method of laser ablation (LIBS) make possible to separate the surface layer element content from the elemental composition of its core. In every LIBS spectrum it is possible to collect tens of thousands of data almost immediately. For efficient analysis of so complex information, it is necessary to use appropriate methods of multivariate analysis, which take into account all variables from entire spectrum, where superfluous and correlated information are rejected and only the most important ones are used [6,7].

2. Results and Discussions

We analyzed two ancient bronze coins. One of them, shown in Figure 1(a), was made in the Pharos mint in the second century BC, during the reign of the Illyrian king Ballaios. The other one was made in the Thesalonica mint in the third century AD, during the reign of Constantine I the Great, and it is shown in Figure 1(b).

Figure 1 (a) *Bronze coin made in the Pharos mint in the second century BC (sample A) (b) Bronze coin made in the Thesalonica mint in the third century AD (sample B)*

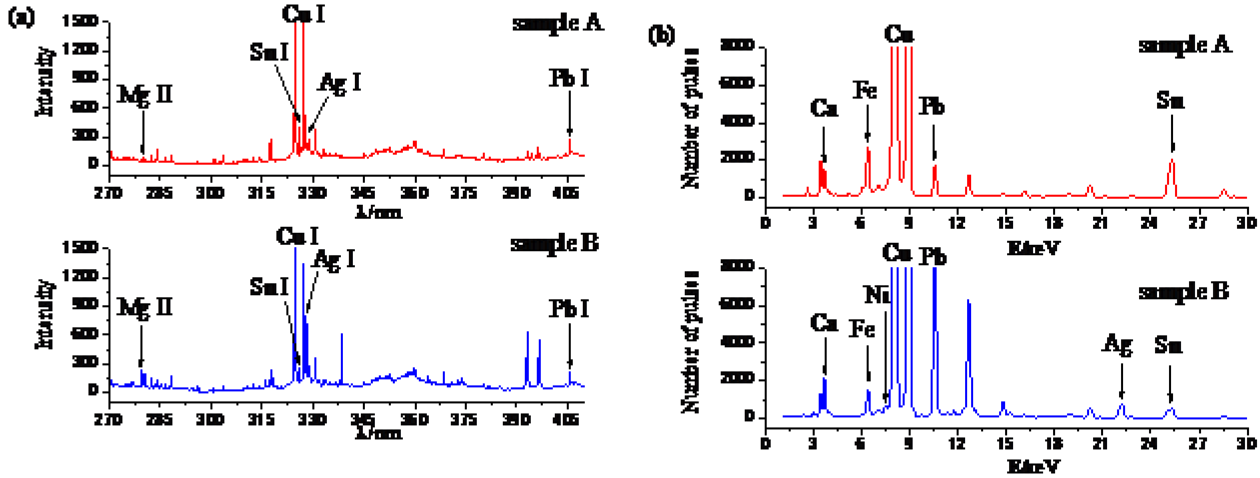

***Figure 2 (a)** LIBS spectrum in the wavelength range from 270 nm to 410 nm obtained during 120 s (b) Characteristic XRF spectra obtained during 600 s.*

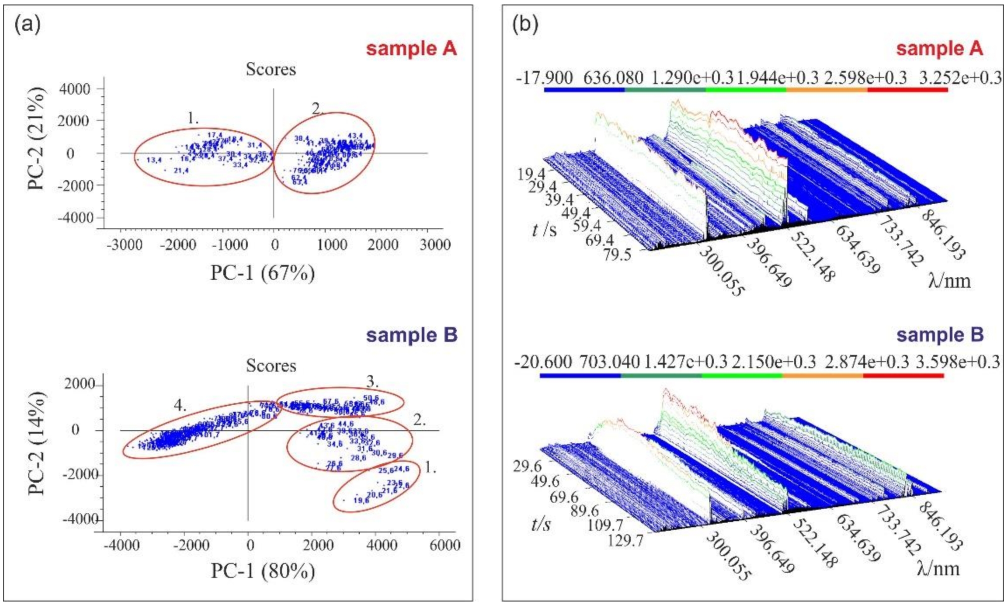

***Figure 3.** Comparison of the effect of different environment- and structure-dependent parameters (a) PCA analysis of experimental data obtained by the LIBS method. (b) 3D view of LIBS spectra obtained during 120 s.*

In order to have a more precise qualitative analysis about elemental composition of chosen samples, we compared the spectra obtained using the method of laser ablation (Figure 2(a)) with those obtained using fluorescence of characteristic x-rays (Figure 2(b)). The main component of experimental setup for measuring emission of laser induced plasma from ablation cloud of our samples are following: Nd:Yag laser, optical system, the target and the spectrometer connected to the computer. Emission XRF spectra, used here, were generated by x-ray tube with rhodium anode. Both methods indicate the existence of the same elements in the same proportions in the respective samples.

As can be seen in Figure 2(a) and Figure 2(b) the sample B, which originates from the 3rd century AD, contains a certain amount of silver, while this element in the sample A from the 2nd century BC, there is no trace.

The spectroscopic data obtained using LIBS method consist of several thousand variables mostly autocorrelated. We have used multivariate PCA method for reducing of dimensionality and classification of data set (Figure 3(a)). In Figure 3(b) is presented the 3D view of 120 LIBS spectra.

Using multivariate PLS method we created a calibration model applicable in analyzing of our (unknown) samples. Namely, the quantitative analysis of experimental data obtained using the LIBS method was performed by means of PLS. We have used seven standard samples with copper concentration in the range from 70% to 90%. This analysis gave the concentration of copper approximately 90% for the sample A and approximately 85% for the sample B. The results are in very good agreement with those obtained after analyzing the experimental XRF spectra, where we used excitation by radioactive ^{109}Cd source.

3. Conclusions

The exploration of copper alloy coins is very important for the history of numismatics and broader aspects of history of economy, such is for example exploitation of resources and transfer of technology. Similarities and differences in the elemental composition of the analyzed samples, one of which dates from 2nd century BC, and the second from 3rd century AD may indicate some of these aspects. The investigation shows that LIBS as well as XRF are suitable methods in analyses of historical and cultural heritage samples. The application of PCA and PLS methods of multivariate analysis is important for more complete analysis and better understanding of spectral data.

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